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Synthesis and characterization of new polyamides bearing 1,1'-thiodi (2-methoxy-3-naphthoyl) structure in the main chain: Microwave synthesis, nanostructures

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ABSTRACT

New polyamides containing 1,1'-thiodi (2-methoxy-3-naphthoyl) structure were prepared under microwave irradiation using Yamasaki phosphorylation method and their solubility, thermal behavior and viscosity were evaluated. The structures of polymers were characterized using IR, ¹H NMR spectroscopy and elemental analysis. These polyamides showed good solubility, viscosity, high thermal stability and glass transition temperatures. Their viscosities are in the range of 0.69-0.85. Their glass transition temperatures are in the range of 189-237 °C. Thermal stabilities for 10% weight loss (T₁₀) are 187-218 °C and for 50% weight loss (T₅₀) are in the range of 476-512 °C. The study of surface morphology showed nanoparticles and nanostructures. © 2012 Trade Science Inc. - INDIA

KEYWORDS

Polyamide;
Microwave irradiation
(MW);
1,1'-thiodi (2-hydroxy-3-naphthoic acid);
Nanostructure;
Nanoparticle;
Aramid.

INTRODUCTION

Aromatic polyamides (aramides) explore high thermal stability, good chemical resistance, and excellent mechanical properties that have broad applications in many areas of research and engineering^[1-3]. However, all of these polymers have the main problem of being difficult to process and fabrication because of their infusibility and low solubility in organic solvents. The reasons are strong interchain forces and interactions, inherent macromolecular rigidity, or crystallinity.

There has been, an increased attention in the preparation of polyamides with different substituents or structural irregularities to improve their processability without lowering their other desired properties. These stud-

ies include entering flexible adducts into the polymer main chain^[4-6], replacing symmetrical aromatic rings by unsymmetrical ones^[7,8], introducing bulky and reliable pendant groups to minimize crystallization^[9-13], and forming a non-coplanar and nonsymmetrical structure^[14,15].

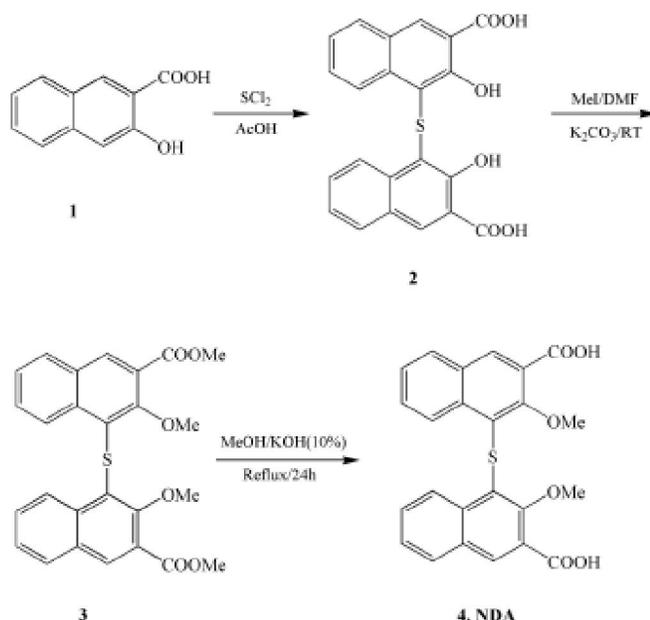
Since the first published reports on the use of microwave irradiation to improve chemical transformations by the research groups of Gedye and Giguere/Majetich in 1986^[16], a large number of articles have been published in this active field, today referred to as microwave-assisted organic synthesis (MAOS)^[17,18]. In a large number of these published articles, microwave heating has been shown to reduce reaction times, increase product yields, and enhance product purities

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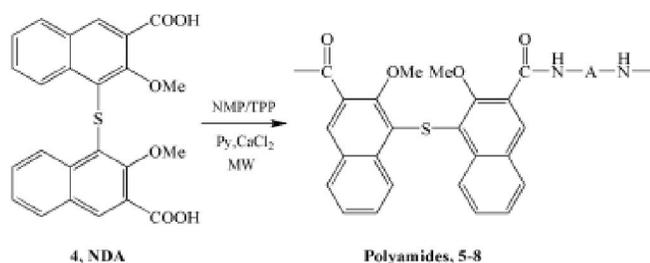
by reducing byproducts compared to conventional heating procedures. The advantages of this strong and wonderful technology have more in recent years also been explored in the context of multistep total synthesis^[19], medicinal chemistry and drug discovery^[20]. Also, these methods was used in a series of fields such as polymer synthesis^[21], material sciences^[22], nanotechnology^[23], and biochemical processes^[24]. The use of microwave irradiation in polymer chemistry has thus become such a popular technique in the scientific community that it

might be assumed that, in a few years, most chemists will probably use microwave energy to heat chemical reactions on a laboratory scale to prepare a large number of polymers^[25]. This efficient method of organic synthesis has been used in a large number of polymer reactions such as, step-growth polymerization for the preparation and synthesis of polyamides^[26], polyimides^[27], poly(amide-imide)s^[28], polyesters^[29] polyurea and polythiourea^[30]. Also, chain growth polymerization under microwave (MW) irradiation as an important polymer synthesis procedure, has been applied for the synthesis of a large number of polymers and macromolecules^[31].

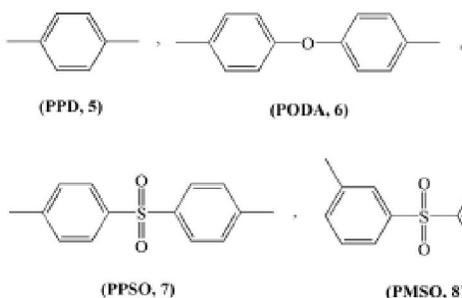
In this research work new polyamides containing 1,1'-thiodi (2-methoxy-3-naphthoyl) units in the main chain were synthesized under microwave irradiation and characterized. They are soluble in a series of organic solvents and showed thermal resistance. SEM images of these polymers showed nanoparticles and nanostructures.



Scheme 1 : Synthesis of monomer (4, NDA).



A (Polyamide):



Scheme 2 : Synthesis of polyamides (5-8).

XL30 (Philips) apparatus. The MicroSYNTH system of Milestone which is a multi-mode platform and equipped with a magnetic stirring plate was used for the microwave synthesis. Inherent viscosities ($\eta_{inh} = \ln \eta_r/c$ at a concentration of 0.5 g dL^{-1}) were measured with an Ubbelohde suspended-level viscometer at 30°C using DMSO as solvent. Thermogravimetric analysis (TGA) were recorded on a V 5.1A DuPont 2000 system under argon atmosphere at a heating rate of $10^\circ\text{C Min}^{-1}$, and differential scanning calorimetry (DSC) recorded on a V 4.OB DuPont 2000 system under argon atmosphere at a heating rate of $10^\circ\text{C Min}^{-1}$.

Synthesis of 1,1'-thiodi (2-methoxy-3-methylnaphthoate) (3)

To DMF (30 mL) were added 1,1'-thiodi (2-hydroxy-3-naphthoic acid) (2^{1321} , 1 mmol, 0.406 g), Na_2CO_3 (4 mmol, 0.40 g), NaI (catalytic) and methyl iodide (4 mmol, 0.25 mL, Caution!) at room temperature. The reaction mixture was stirred at room temperature for 24 hours. After completion of the reaction (monitored by TLC), water was added and extracted with chloroform ($3 \times 30 \text{ mL}$). The combined organic layers were dried (Na_2SO_4) and evaporated to afford a white solid which was recrystallized in ethanol to obtain diester (3) in 94% yield and melting point of $181\text{--}182^\circ\text{C}$. IR (KBr) vcm^{-1} : 2950, 1720 (C=O), 1488, 1442, 1285, 1230, 1008, 790. $^1\text{H NMR}$ (500 MHz, DMSO- d_6) δ : 2.74 (s, 3H), 2.91 (s, 3H), 3.67 (s, 6H), 7.46 (dd, 2H, $J=5, 10 \text{ Hz}$), 7.57 (dd, 2H, $J=5, 10 \text{ Hz}$), 8.04 (d, 2H, $J=10 \text{ Hz}$), 8.29 (s, 2H), 8.59 (d, 2H, $J=10 \text{ Hz}$) ppm. $^{13}\text{C NMR}$ (125 MHz, DMSO- d_6) δ : 168.66, 158.37, 136.54, 134.42, 131.47, 130.58, 129.73, 127.86, 126.95, 126.28, 125.54, 63.84, 37.54 ppm. MS (EI) m/z (relative intensity %): 462 $[\text{M}]^+$ (100%), 415 (74%), 185 (14%), 357 (22%), 286 (21%), 258 (26%), 229 (27%), 187 (34%), 169 (28%), 145 (71%), 115 (77%), 59 (82%), 45 (83%). Analytical calculated for $\text{C}_{26}\text{H}_{22}\text{O}_6\text{S}$ ($M=462.51$): C, 67.52%; H, 4.79%; Found, C, 67.55%; H, 4.78%.

Synthesis of 1,1'-thiodi (2-methoxy-3-naphthoic acid) (4, NDA)

To the mixture of 3 (1 mmol, 0.46 g) and methanol (10 mL) was added KOH solution (10%, 50 mL) at room temperature. The mixture was stirred at room tem-

perature for 2h and then was refluxed for 24h. After completion of the reaction (monitored by TLC), water was added and the mixture was neutralized using HCl (10%) solution. The resulting precipitate left for 12h and then filtered to afford the crude product that recrystallized in ethanol to obtain diacid (4, NDA) as a white precipitate in 95% yield and melting point of $286\text{--}287^\circ\text{C}$. IR (KBr) vcm^{-1} : 3500, 2933, 2362, 1685 (C=O), 1446, 1280, 1001, 754. $^1\text{H NMR}$ (500 MHz, DMSO- d_6) δ : 3.64 (s, 6H), 7.52 (dd, 2H, $J=5, 10 \text{ Hz}$), 7.62 (dd, 2H, $J=5, 10 \text{ Hz}$), 8.02 (d, 2H, $J=10 \text{ Hz}$), 8.34 (s, 2H), 8.56 (d, 2H, $J=10 \text{ Hz}$), 13.09 (b, 2H) ppm. $^{13}\text{C NMR}$ (125 MHz, DMSO- d_6) δ : 167.76, 157.26, 136.43, 133.30, 130.44, 130.34, 129.62, 126.94, 126.72, 126.05, 125.93, 62.95 ppm. MS (EI) m/z (relative intensity %): 434 $[\text{M}]^+$ (100%), 388 (51%), 343 (18%), 258 (26%), 202 (17%), 173 (23%), 145 (54%), 115 (68%), 63 (22%), 45 (51%). Analytical calculated for $\text{C}_{24}\text{H}_{18}\text{O}_6\text{S}$ ($M=434.46$): C, 66.35%; H, 4.18%; Found, C, 66.31%; H, 4.19%.

Synthesis of polyamides

Polyamides were synthesized through the phosphorylation reaction of 1,1'-thiodi (2-methoxy-3-naphthoic acid) (4, NDA) with various diamines as shown in Scheme 2. A typical example for the preparation of polyamides is given. A mixture of 4 (1 mmol, 0.432 g), *p*-phenylenediamine (1 mmol, 0.11 g), 0.3 g of CaCl_2 , 0.6 mL of TPP, 0.5 mL of pyridine, and 4 mL of NMP were added to the quartz tube and irradiated under microwave in 600W for 9 Min. ($3 \times 3 \text{ Min.}$) and the rest time of 10 Min. ($2 \times 5 \text{ Min.}$). After cooling to room temperature, the resulting viscose reaction mixture was poured into 300 mL of boiling methanol. The resulting crude product was precipitated and then filtered. The resulting polymer was washed with hot methanol (50 mL), hot water (twice, 50 mL) and then hot methanol (50 mL), respectively; and dried under vacuum at 100°C overnight. The yields were almost quantitative. Spectral data, thermal properties, viscosity and solubility of these polyamides were reported in the following TABLES and Figures.

RESULTS AND DISCUSSION

In this research work, we wish to report the syn-

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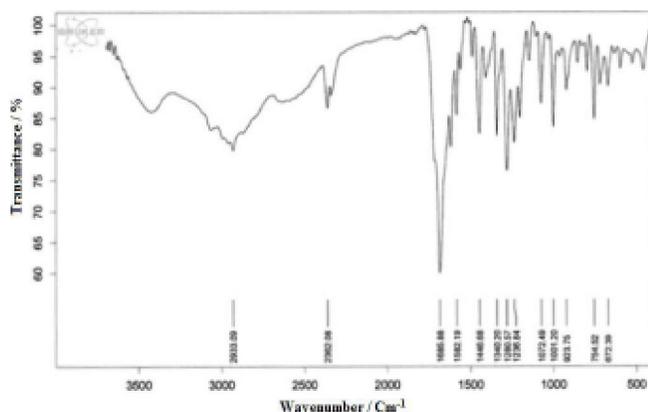


Figure 1 : FT-IR spectrum of diacid (4, NDA).

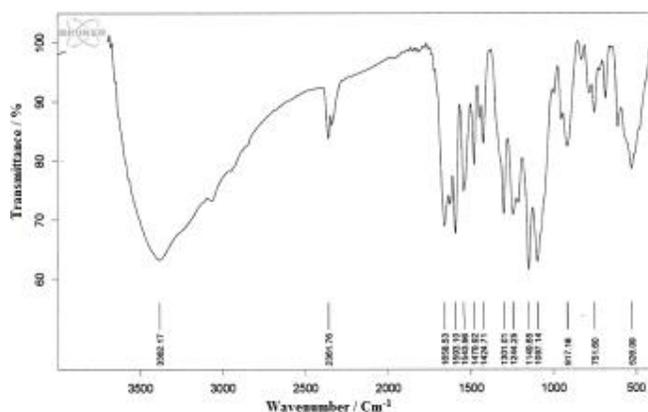


Figure 2 : FT-IR spectrum of polyamide (8, PMSO).

TABLE 1 : Inherent viscosity and the yields of polyamides.

Polymer	Yield (%)	$\eta_{inh}(\text{g/dL})^a$
PPD (5)	95	0.76
PODA (6)	93	0.69
PPSO (7)	97	0.81
PMSO (8)	96	0.85

^aMeasured at a polymer concentration of 0.5 g/dL in DMSO solvent at 30 °C.

thesis and characterization of polyamides obtained from the reaction of a new monomer (4, NDA), containing 1,1'-thiodi (2-methoxy-3-naphthoyl) units, and aromatic diamines under microwave irradiation. 2 was prepared according to the reported procedure from the reaction of 1 and sulfur dichloride (SCl_2)^[32]. 3 was prepared from the reaction of 2 and methyl iodide in DMF at room temperature. The corresponding diacid (4, NDA) was synthesized through hydrolysis of diester using MeOH/KOH (10%) at reflux conditions. The IR spectrum of diacid (4, NDA) is appeared in Figure 1. Polymerization were performed using Yamasaki phosphorylation reaction of diacid and diamines in the

presence of triphenylphosphite (TPP), pyridine (Py), N-methylpyrrolidinone (NMP) and calcium chloride (CaCl_2) under microwave irradiation almost in quantitative yields (TABLE 1). Polymers were precipitated in boiling methanol and washed with hot water and methanol respectively. The IR and ¹H NMR spectra of polyamides were showed the correct structures (TABLE 2). The IR spectra of polyamide 8 (PMSO) is appeared in Figure 2; and showed the corresponding structure according to the main functional groups. The inherent viscosities and the yields of polyamides were reported in TABLE 1.

The solubility behavior of polyamides was investigated qualitatively in a series of organic solvents such as N-methylpyrrolidinone (NMP), N, N-dimethylformamide (DMF), tetrahydrofuran (THF), dimethylsulfoxide (DMSO), N,N-dimethylacetamide (DMAc) and *m*-cresol, and the results are summarized in TABLE 3. All the polymers showed reliable solubil-

TABLE 2 : Spectral data of polymers.

Polymer	IR (vcm^{-1})	¹ H NMR (500 MHz, DMSO- d_6): δ (ppm)
PPD (5)	3408 (NH), 3056, 2985, 1640 (C=O), 1514, 1103, 738	2.69 (s, 6H), 7.33 (s, 2H), 7.37 (dd, 2H, J= 8, 10 Hz), 7.48 (dd, 2H, J= 8, 10 Hz), 7.51 (b, 4H), 8.03 (d, 2H, J= 10 Hz), 8.44 (d, 2H, J= 10 Hz), 10.76 (s, 2H).
PODA (6)	3388 (NH), 3055, 2465, 1687 (C=O), 1499, 1217, 1069	2.69 (s, 6H), 7.08 (d, 3H, J= 10 Hz), 7.33 (s, 2H), 7.36 (dd, 2H, J= 8, 10 Hz), 7.51 (dd, 2H, J= 8, 10 Hz), 7.77 (t, 5H, J= 10 Hz), 7.92 (d, 5H, J= 10 Hz), 8.51 (s, 2H).
PPSO (7)	3391 (NH), 3078, 2956, 2364, 1667 (C=O), 1591, 1548, 1247, 1146, 1095, 922	2.68 (s, 6H), 6.62 (d, 2H, J= 10 Hz), 7.32 (s, 2H), 7.35 (dd, 2H, J= 9, 10 Hz), 7.50 (dd, 2H, J= 9, 10 Hz), 7.54 (d, 2H, J= 10 Hz), 7.75 (d, 2H, J= 10 Hz), 7.84 (d, 2H, J= 9, 10 Hz), 7.91-8.02 (m, 4H), 8.40 (d, 2H, J= 6 Hz), 10.83 (s, 1H), 10.89 (s, 1H).
PMSO (8)	3382 (NH), 3086, 2963, 2361, 1656 (C=O), 1593, 1301, 1097, 917, 751, 526	2.69 (s, 6H), 7.29 (s, 2H), 7.33 (dd, 2H, J= 8, 10 Hz), 7.38 (dd, 2H, J= 8, 10 Hz), 7.46 (dd, 2H, J= 8, 10 Hz), 7.54 (dd, 2H, J= 1.5, 8 Hz), 7.69 (dd, 2H, J= 1.4, 9 Hz), 8.23 (s, 2H), 8.41 (d, 2H, J= 8 Hz), 10.79 (s, 2H).

ity in polar organic solvents. This might be due to the presence of naphthalene units which decreased intermolecular and intramolecular hydrogen bonding but methoxy groups increases the intramolecular hydrogen bonding and flexibility and then decrease the crystallinity and close packing. On the other hand, naphthalene units reduced the flexibility and increased close packing and crystallinity. Also, the aromatic diamine structure varies the solubility. According to the above discussions the solubility of polyamides were affected by the several variables and the solubility varies according to the structure of diacid monomer (4) and aromatic diamines. The viscosities of polyamides were measured in DMSO at 30 °C and are in the range of 0.69-0.85 (TABLE 1).

The thermal stability of polyamides was evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The entire polymers showed good thermal stability, the results are summarized in TABLE 4 and for one sample is showed in Figure 3. Glass transition temperatures (T_g) of polyamides were evaluated by differential scanning calorimetry (DSC) and are in the range of 189-237 °C. The results are summarized in TABLE 4. According to the structure of diamine, insertion of the ether group in the diamine structure is increased the overall flexibility of the polymer chains and decreased the T_g value. The

TABLE 3 : Elemental Analysis of polymers.

Polymer	Formula	Elemental Analysis					
		Calculated (%)			Found (%)		
		C	H	N	C	H	N
PPD	$C_{32}H_{22}N_2O_4S$	72.44	4.18	5.28	72.49	4.20	5.33
PODA	$C_{36}H_{26}N_2O_5S$	72.22	4.38	4.68	72.26	4.39	4.74
PPSO	$C_{36}H_{26}N_2O_6S_2$	66.86	4.05	4.33	66.82	4.08	4.39
PMSO	$C_{36}H_{26}N_2O_6S_2$	66.86	4.05	4.33	66.79	4.07	4.37

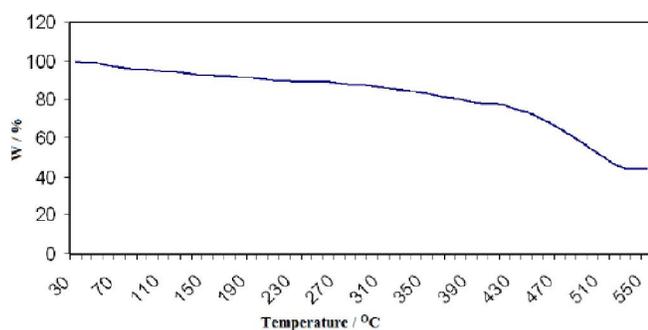


Figure 3 : TGA of polyamide (PODA, 6).

TABLE 4 : Thermal properties of polyamides.

Polymer	T_g (°C)	T_{10}^a (°C)	T_{50}^b (°C)	Char yields ^c (%) _{580 °C}
PPD (5)	216	204	512	47
PODA (6)	189	187	507	43
PPSO (7)	231	211	476	31
PMSO (8)	237	218	495	37

^aTemperature of 10% weight loss determined in argon atmosphere; ^bTemperature of 50% weight loss determined in argon atmosphere; ^cChar yield calculated as the percentage of solid residue after heating from room temperature to 580 °C under argon.

TABLE 5 : The solubility of polyamides.

Polymer	NMP	DMAc	DMF	DMSO	m-Cresol	THF
PPD (5)	++	++	++	++	±	+
PODA (6)	++	++	++	++	+	+
PPSO (7)	++	++	++	++	-	-
PMSO (8)	++	++	++	++	-	-

(++) Soluble at room temperature; (+) soluble upon heating; (±) partially soluble; ^aSolubility measured at a polymer concentration of 0.05 g/ml.

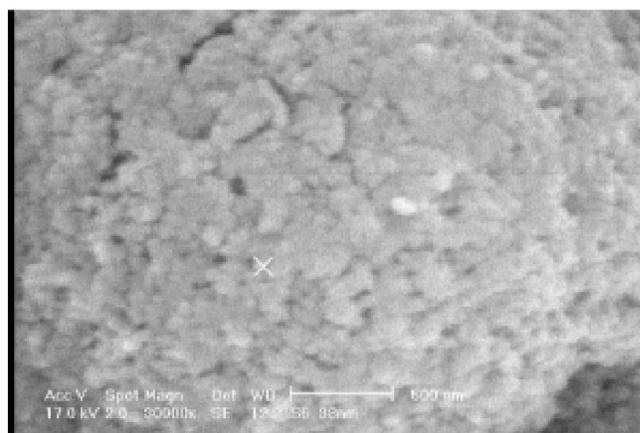


Figure 4 : SEM image of polyamide (5, PPD).

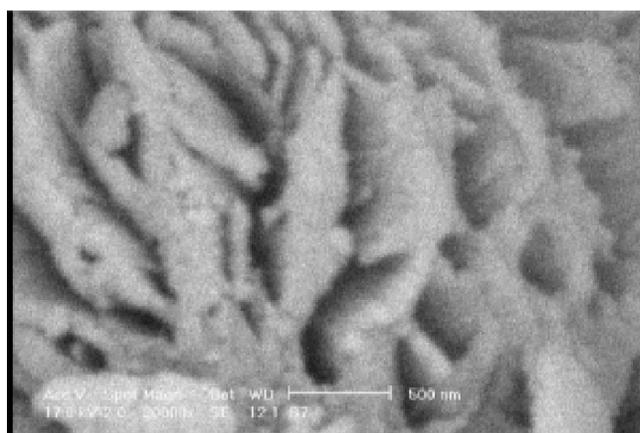


Figure 5 : SEM image of polyamide (6, PODA).

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Figure 6 : SEM image of polyamide (7, PPSO).

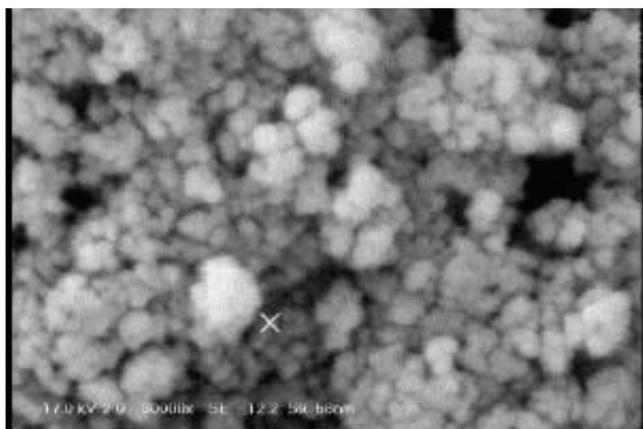


Figure 7 : SEM image of polyamide (8, PMSO).

polymers containing diamines without other flexible groups (such as naphthalene and meta and para benzene derivatives) have high T_g , because of the lower flexibility of the overall polymer chains.

The thermal stability of these polymers was studied by thermogravimetric analysis (TGA). All the polymers showed good thermal stability, their decomposition at argon atmosphere for temperature of 10% weight loss $T(10)$ was in the range of 187-218 °C and the temperature of 50% weight loss $T(50)$ was in the range of 476-512 °C which indicates excellent thermal stability in the prepared polymers. The polymer decomposition temperature for various percent of decomposition and char yield at 580 °C for all polymers are summarized in TABLE 4. According to the obtained data for thermal stability, the incorporation of benzene units into the polymers backbone enhanced the thermal stability.

The surface morphology of polymers was evaluated using their SEM images (Figures 4, 5, 6 and 7).

According to these images two polyamides (5 and 8) have shown particle structures and on the other hand 6 and 7 have shown continues structure.

CONCLUSIONS

A series of new polyamides based on the methoxynaphthoic acid were successfully obtained through the direct polycondensation reaction of a thiodi(2-methoxy-3-naphthoic acid) with various diamines via Yamazaki method under microwave irradiation (MW). The polymers showed reliable solubility and high thermal stability. This is due to the presence of naphthalene and methoxy groups in the presence of tetrahedral sulfide functional group. The presence of ether group in the diamine decreased glass transition temperature and polymers with higher symmetric and rigid structures in the diamine and as a result in the overall polymer chains showed the higher thermal stability. Thus, we afforded polyamides with improved solubility and high heat resistance. The study of surface morphology of polyamides showed nanoparticles and nanostructures.

REFERENCES

- [1] S.Jamshidi, H.Yeganeh, S.Mehdipour-Ataei; *Polym.Int.*, **60**, 126 (2011).
- [2] D.J.Yoo, S.H.Hyun, A.R.Kim, G.G.Kumar, K.S.Nahm; *Polym.Int.*, **60**, 85 (2011).
- [3] J.Borah, C.S.Wang; *Chin.J.Polym.Sci.*, **28**, 107 (2010).
- [4] X.Yu, X.Zhao, C.Liu, Z.Bai, D.Wang, G.Dang, H.Zhou, C.Chen; *J.Polym.Sci.Part A: Polym.Chem.*, **48**, 2878 (2010).
- [5] D.J.Liaw, B.Y.Liaw, C.W.Yu; *Polymer*, **42**, 5175 (2001).
- [6] M.Ghaemy, M.Barghamadi; *J.Appl.Polym.Sci.*, **110**, 1730 (2008).
- [7] S.H.Hsiao, C.W.Chen, G.S.Liou; *J.Polym.Sci.Part A: Polym.Chem.*, **42**, 3302 (2004).
- [8] R.R.Pal, P.S.Patil, M.M.Salunkhe, N.N.Maldar, P.P.Wadgaonkar; *Eur.Polym.J.*, **45**, 953 (2009).
- [9] M.Ghaemy, M.Barghamadi; *J.Appl.Polym.Sci.*, **114**, 3464 (2009).
- [10] P.Blondin, J.Bouchard, S.Beapre, M.Belletete, G.Durocher, M.Leclerc; *Macromolecules*, **33**, 5874 (2000).
- [11] S.H.Chen, C.S.Shiau, L.R.Tsai, Y.Chen, *Polymer*,

- 47, 8436 (2006).
- [12] D.J.Liaw, W.H.Chen; *Polymer*, **44**, 3865 (2003).
- [13] H.J.Yen, G.S.Liou; *J.Polym.Sci.Part A: Polym.Chem.*, **46**, 7354 (2008).
- [14] M.Ghaemy, R.Alizadeh; *Reac.Func.Polym.*, **71**, 425 (2011).
- [15] Y.L.Liu, S.H.Tsai; *Polymer*, **43**, 5757 (2002).
- [16] R.Gedye, F.Smith, K.Westaway, H.Ali, L.Baldisera, L.Laberge, R.Rousell; *Tetrahedron Lett.*, **27**, 279 (1986).
- [17] P.Lidström, J.P.Tierney, Eds.; 'Microwave-Assisted Organic Synthesis', Blackwell Publishing, Oxford, U.K., (2005).
- [18] B.A.Roberts, C.R.Strauss; *Acc.Chem.Res.*, **38**, 653 (2005).
- [19] D.D.Artman, A.W.Grubbs, R.M.Williams; *J.Am.Chem.Soc.*, **129**, 6336 (2007).
- [20] C.O.Kappe, D.Dallinger; *Nature Rev.Drug Discov.*, **5**, 51 (2006).
- [21] R.Hoogenboom, U.S.Schubert; *Macromol.Rapid Commun.*, **28**, 368 (2007).
- [22] J.Perelaer, B.J.De Gans, U.S.Schubert; *Adv.Mater.*, **18**, 2101 (2006).
- [23] A.Burya, O.Kuznetsova, A.Konchits, A.Redchuk; *Materials Science Forum*, **674**, 189 (2011).
- [24] J.M.Collins, N.E.Leadbeater; *Org.Biomol.Chem.*, **5**, 1141 (2007).
- [25] T.N.Glasnov, C.O.Kappe; *Macromol.Rapid Commun.*, **28**, 395 (2007).
- [26] S.Mallakpour, M.Taghavi; *Polymer J.*, **40**, 1049 (2008).
- [27] S.Mallakpour, Z.Rafiee; *Iran.Polym.J.*, **17**, 907 (2008).
- [28] H.N.Isfahani, K.Faghihi, M.Hajibeygi, M.Bokaei; *Polym.Bull.*, **64**, 633 (2010).
- [29] S.Sinnwell, H.Ritter; *Aust.J.Chem.*, **60**, 729 (2007).
- [30] A.Banihashemi, H.Hazarkhani, A.Abdolmaleki; *J.Polym.Sci., Part A: Polym.Chem.*, **42**, 2106 (2004).
- [31] C.Holtze, M.Antonietti, K.Tauer; *Macromolecules*, **39**, 5720 (2006).
- [32] a) W.S.Gump, J.C.Vitucci; *J.Am.Chem.Soc.*, **67**, 238 (1945); b) M.Gazdar, S.Smiles; *J.Chem.Soc.*, **97**, 2248 (1910).